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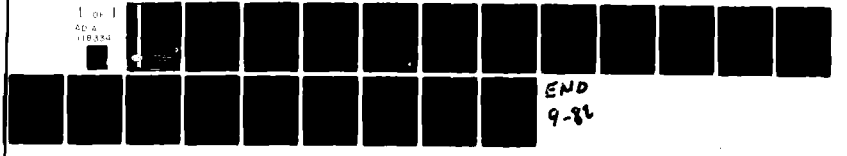

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Report 2360

IDENTIFICATION OF DRYING OILS IN PAINTS BY GAS-LIQUID CHROMATOGRAPHY

by

Laurie Herriott

June 1982

U.S. ARMY MOBILITY EQUIPMENT
RESEARCH AND DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This gas-liquid chromatographic method is for the identification of drying oils in paint. The identification is made from the distribution of fatty acids as methyl esters shown on the chromatogram.

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PREFACE

The work covered by this report was performed by Laurie Herriott and was reviewed by Troy Nichols under the supervision of Emil J. York, Chief, Material Technology Laboratory. The effort constitutes a part of the U.S. Army Materials and Mechanics Research Center's program to provide better procedures in chemical testing techniques to increase inspection efficiency for products procured by the U.S. Army Materiel Development and Readiness Command.

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ILLUSTRATIONS

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IDENTIFICATION OF DRYING OILS IN PAINTS

BY GAS-LIQUID CHROMATOGRAPHY

I. INTRODUCTION

1. Purpose. The purpose of this investigation was to revise and update Federal Test Method Standard (FTMS) 7501, "Identification of Drying Oils (Gas-Liquid Chromatography)."

2. Background. Some of the military specifications for paints specify that certain drying oils are to be used in the formulation. If those drying oils are not used, the paint will prove unsatisfactory in its intended application. Therefore, it is essential for purposes of quality control that an accurate method be available for the identification of these drying oils. In September 1965, Method 7501 of FTMS 141 was approved for this purpose, but it has since been shown to be lacking in necessary flexibility for application to actual samples of specification paints.

II. DETAILS OF TESTS

3. Reagents.

a. Boron Trifluoride solution[1]—add 23 ml of boron fluoride methyl ether slowly to 150 ml of chilled absolute methyl alcohol in a 200-ml volumetric flask and dilute the volume with absolute methanol. Stopper tightly and store in a refrigerator. Discard after one month.

b. Petroleum Ether.[2]

4. Gas-Liquid Chromatographic Column. Prepare a 6-ft by 1/8-in. glass column, packed with 20-percent diethylene glycol succinate on 60-80 mesh chromosorb W acid washed (WAW). Using the thermal conductivity detector (TCD), condition the column at 200° C with helium at a flow rate of 60 ml/min, until the baseline is stabilized.

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[1] L. D. Metcalfe and A. A. Schmitz, J. Am. Oil Chem. Soc., 33, 361 (1961).

[2] L. D. Metcalfe, A. A. Schmitz, and J. R. Pelka, Anal. Chem., 38, 514 (1966).

5. Sample Preparation. Isolate the fatty acids from the resin or oil by saponification, acid hydrolysis, and solvent separation as in FTMS 7021 and FTMS 7031. If the fatty acids have become solid, warm them slightly. Then, accurately weigh about 0.2 g in a *6-in. screw cap* test tube. Add 6 ml of the Boron Trifluoride solution and immerse in a 65° to 70° C water bath for 10 min. Transfer to a separatory funnel with 20 ml water and 30 ml of petroleum ether. Shake gently. Discard the bottom water layer and filter the remaining layer through fast filter paper into a 50-ml beaker and evaporate in a 65° to 70° C water bath to about 2 ml. Do not evaporate to dryness. Transfer and store in a closed 2-ml vial. Monitoring the specification or statement of composition, inject 1.5 ml of the prepared methyl esters using the optimum conditions for each oil as shown in Table 1.

Table 1. Drying Oils Used in Sample Preparation

Drying Oils	Column Temperature (° C)	Carrier (Helium) Flow (ml/min)
Castor	20 min at 170°; 50 min at 200°; rate 20° C/min	60
Soya	180	60
Cottonseed	180	60
Linseed	180	50
Safflower	190	40

Thermal conductivity detector 250° C.
Injection port temperature 275° C.

6. Identification of Ester and Oil. The individual methyl esters can be identified by their relative retention times as given in Table 2. The drying oil, itself, may be identified in either of two ways. First, by comparison of its chromatogram with those of known oils. Second, identification of the drying oil may be made by matching concentration of the methyl esters with the values given in Table 3. For this purpose, concentration (Cx) of the methyl ester is calculated as follows:

$$C_x = \frac{A_x}{A_T} \times F_x \times 100.$$

Where A_x is the peak area of the methyl ister; A_T is the total area of the methyl ester peaks; and F_x is a correction factor determined from a known sample.

Table 2. Relative Retention Data of Methyl Esters of Oil Fatty Acids

Ester	Relative Retention Time
Caprylic	0.10
Capric	0.19
Lauric	0.32
Myristic	0.56
Palmitic	1.0
Palmitoleic	1.15
Stearic	1.7
Oleic	1.94
Linoleic	2.31
Linolenic	2.97
Licanic	5.2
Eleostearic	5.3
Ricinoleic	10.0

(Ester of Palmitic Acid = 1)

Table 3. Weight Percent Distribution of Fatty Acids in Unmodified Oil

Oil	Caprylic	Capric	Lauric	Myristic	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic	Linolenic	Licanic	Eleostearic	Ricinoleic
Castor					2		1	7	3				87
Coconut	6	6	44	18	11		6	7	2	t			
Cottonseed		t	t	1	29	2	4	24	40				
Linseed					6	t	4	22	16	52			
Oiticica					7		5	6			78		
Perilla					7		2	13	14	64			
Safflower				t	8	t	3	13	75	1			
Soybean				t	11		4	25	51	9			
Tall					5		3	46	41	3			
Tung					4		1	8	4	3			
Menhaden		t	7	16	16	2	15	7	2				

t = trace

III. RESULTS AND DISCUSSION

The various drying oils used in paints are composed of specific amounts of fatty acids as given in Table 3. Determination of these fatty acids as methyl esters by gas-liquid chromatography provides a means for confirmation of the required drying oil in the paint.

Because of the wide variation of composition of drying oils it was impractical, if not impossible, to develop a single chromatographic program for satisfactory identification for all of the oil acids. Carrier flow rate and column oven temperature were adjusted for optimum resolution of the methyl esters for each drying oil.

The one complete method for identification of the oil acid consists of the following steps. The acid is saponified and extracted with water as the sodium salt from an ethyl ether despersion of the paint vehicle. On acidification with hydrochloric acid, the fatty acid is then extracted with chloroform (FTMS 7021). Evaporation[1] [2] follows with conversion of the fatty acid to the methyl ester with Boron Trifluoride solution. This well-known reaction converts the acid to a more volatile product which can then be determined by gas-liquid chromatography. An example of this reaction is:

$$\underset{\text{Palmitic acid}}{CH_3(CH_2)_{14}COOH} + BF_3\,2CH_3OH \longrightarrow \underset{\text{Methyl palmitate}}{CH_3(CH_2)_{14}COCH_3}.$$

Figure 1 is a chromatogram of the methyl esters of soybean oil obtained with the above procedure. This chromatogram illustrates the use of this method in the identification of drying oils. By its retention time the methyl ester is identified, and by the percentage of each methyl ester, the drying oil is identified.

Figure 2 is the chromatogram of the methyl esters of castor oil. The striking difference between the chromatograms of Figures 1 and 2 illustrate the utilization of this method in identifying drying oils.

V. CONCLUSION

An improved method was developed for the confirmation of the presence of the required drying oil in military specification paints. To a limited extent, the method is useful in the identification of drying oils in nonspecification paints. In some instances, mixtures of drying oils can be determined.

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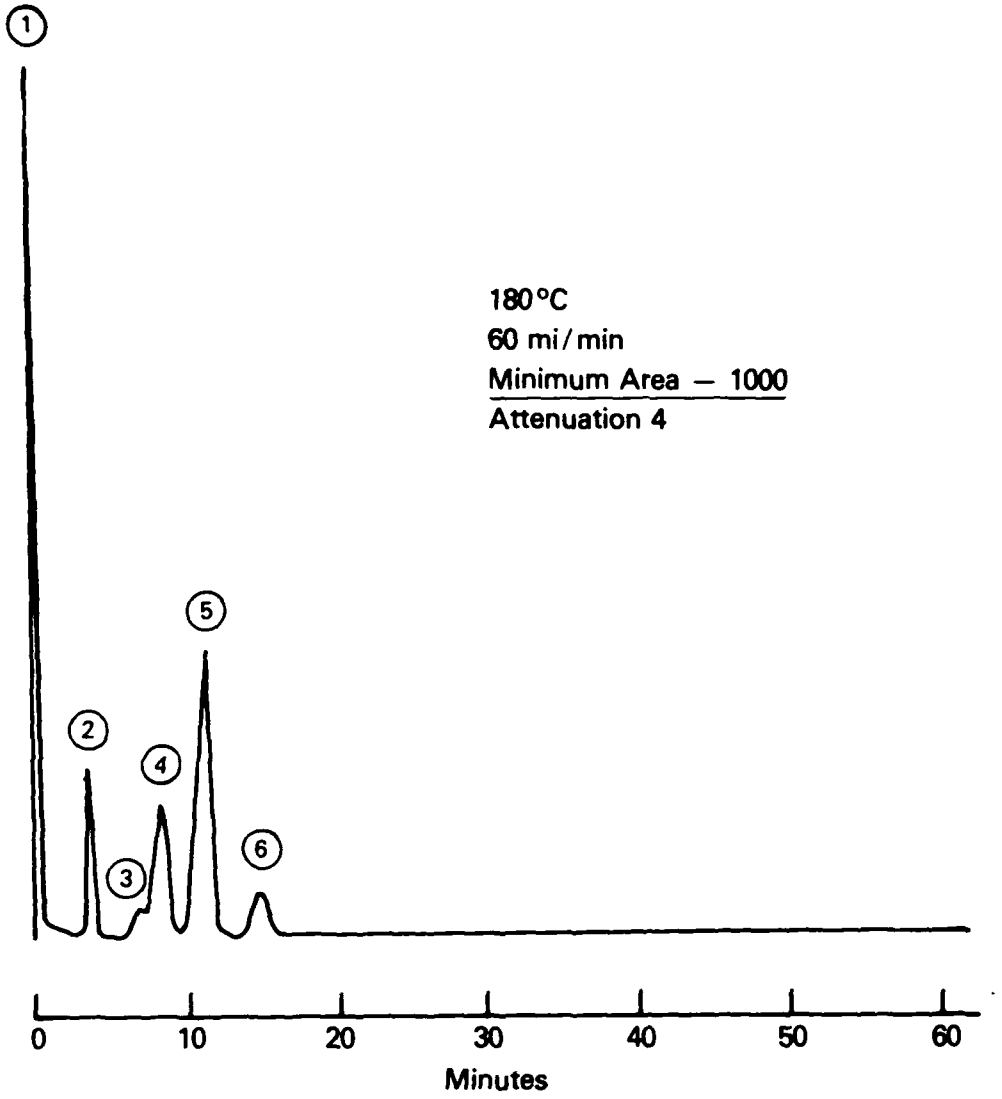
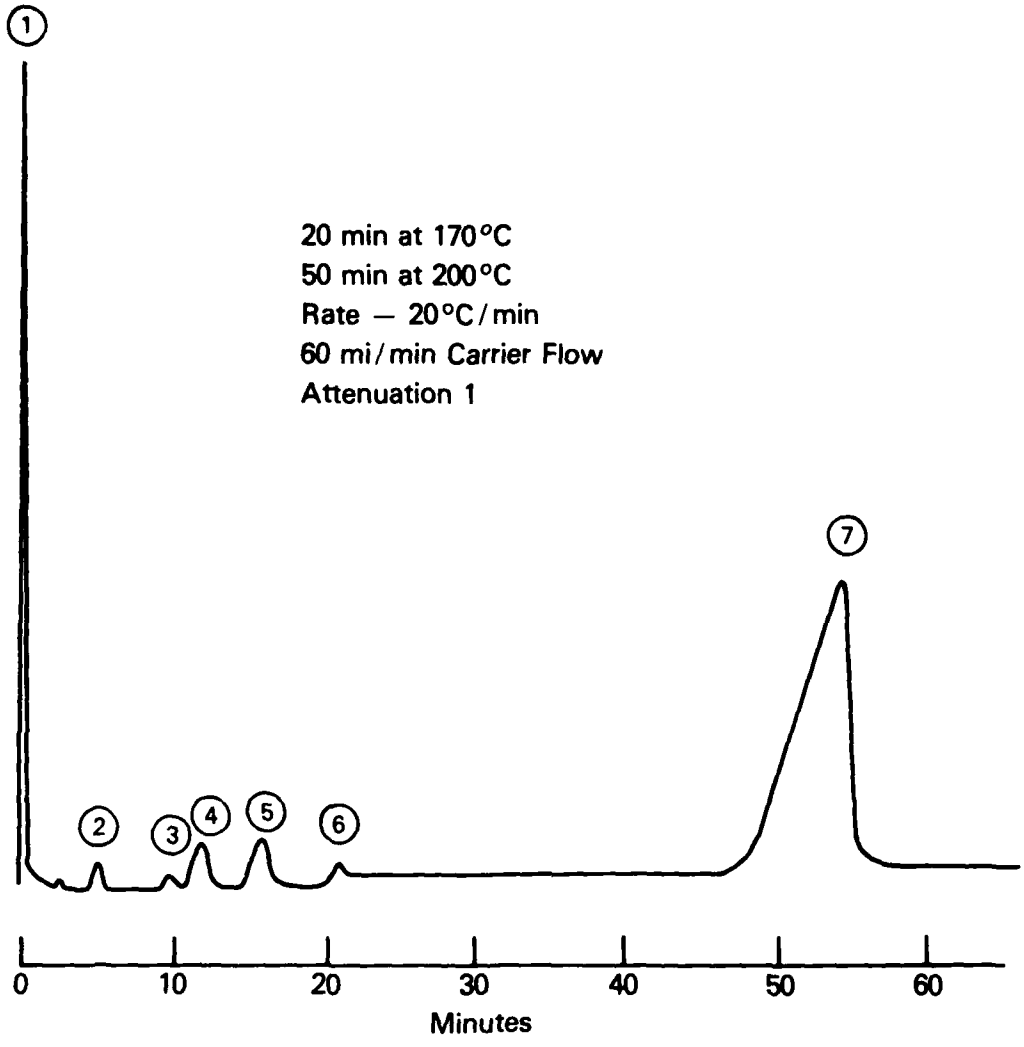
[1] L. D. Metcalfe and A. A. Schmitz, J. Am. Oil Chem. Soc., 33, 361 (1961).

[2] L. D. Metcalfe, A. A. Schmitz, and J. R. Pelka, Anal. Chem., 38, 514 (1966).



1. Petroleum Ether
2. Palmitic
3. Stearic
4. Oleic
5. Linoleic
6. Linolenic

Figure 1. Chromatogram of soybean oil methyl ester.



1. Petroleum Ether
2. Palmitic
3. Stearic
4. Oleic
5. Linoleic
6. Impurity
7. Ricinoleic

Figure 2. Chromatogram of castor oil methyl ester.

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